



# **A Critical Overview of ASP and Future Perspectives of NASP in EOR of Hydrocarbon Reservoirs: Potential Application, Prospects, Challenges and Governing Mechanisms**

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Abstract: Oil production from depleted reservoirs in EOR (Enhanced Oil Recovery) techniques has significantly increased due to its huge demands in industrial energy sectors. Chemical EOR is one of the best approaches to extract the trapped oil. However, there are gaps to be addressed and studied well for quality and cost consideration in EOR techniques. Therefore, this paper addresses for the first time a systematic overview from alkaline surfactant polymer ((ASP)) and future perspectives of nano-alkaline surfactant polymer ((NASP)), its synergy effects on oil recovery improvement, and the main screening criteria for these chemicals. The previous findings have demonstrated that the optimum salinity, choosing the best concentration, using effective nano-surfactant, polymer and alkaline type, is guaranteed an ultra-low IFT (Interfacial Tension). Core flood results proved that the maximum oil is recovered by conjugating nanoparticles with conventional chemical EOR methods (surfactant, alkaline and polymer). This work adds a new insight and suggests new recommendation into the EOR application since, for the first time, it explores the role and effect of nanotechnology in a hybrid with ASP. The study illustrates detailed experimental design of using NASP and presents an optimum micro-model setup for future design of NASP flow distribution in the porous media. The presence of nano along with other chemicals increases the capillary number as well as the stability of chemicals in the solution and strengthens the effective mechanisms on the EOR.

Keywords: nano-alkaline-surfactant-polymer; ASP; EOR; interfacial tension; contact angle; core-flooding

# 1. Introduction

The United States energy information administration has forecasted that worldwide energy use will surge 28% by 2040. Hydrocarbons are regarded as the vital source of energy in the world [1]. Hydrocarbons are recovered in three stages: primary, secondary, and tertiary. Primary oil recovery or natural drive means production of oil due to a change in the production well pressure [2]. Secondary oil recovery starts when the pressure inside the well drops decreases significantly. In the secondary oil recovery reservoir, pressure increased due to fluid (water or gas) injection [3]. Tertiary recovery is used after the secondary stage to displace the trapped oil. Around 33% STOOIP (Stock Tank Oil Original in Place) recovered after primary and secondary methods [4]. After the secondary stage, high oil saturation remains in the reservoir formation [5]. Many oil companies focused on developing new technology at the beginning of 1980; in the US, oil production was expedited after using chemical flooding [6].

Chemical injection as the main EOR process mobilizes the remaining residual oil saturation by improving oil microscopic/macroscopic displacement efficiency [7,8]. Oil microscopic displacement efficiency is improved by surfactant and alkaline injection. Alkaline enhances the trapped oil mobility by adjusting the pH of in situ water [2]. On the other



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**Copyright:** © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). hand, oil macroscopic displacement efficiency is improved by polymer injection. All of the mentioned CEOR (Chemical Enhance Oil Recovery) methods aim to expedite the ultimate oil recovery.

The main limitation of CEOR method is the excessive adsorption at the rock surface. When these chemicals are introduced into the formation for oil recovery optimization, an extreme amount of surfactant and polymer is lost on the rock surface. This challenge makes the process very costly and have low efficiency in wettability alteration and IFT reduction.

Recently, nanoparticles were used as an effective chemical EOR method to reduce surfactant and polymer adsorption, to increase oil recovery by modifying wettability, and to reduce oil viscosity and water oil IFT. Recent works have suggested that using ASP in hybrid effectively improves residual oil production in the reservoir pore throats [9]. Recent advances, methods and technologies of these chemicals have not been summed up in detail. Therefore, a critical review on the role and effect of different types and concentrations of surfactant, polymer, alkaline and hybrid on oil recovery is needed

The main objective of our work is focused on the application of nano-alkaline surfactant polymer in EOR by considering the governing mechanisms of recovery and reservoir conditions. Moreover, the effect and role of hybrid nano-ASP flooding in carbonate and sandstone reservoirs are studied effectively by addressing different EOR mechanisms such as interfacial tension, wettability alteration and mobility control. Accordingly, the following questions would be addressed: (i) Could the new idea and recommendation by utilizing NASP design be successful in providing the multi-functional EOR agents? (ii) What are the advantages and disadvantages of using natural based surfactants in NASP over chemical surfactants, and which kind of surfactant is environmentally-friendly; (iii) What are the main challenges and limitations of ASP? (iv) What are the effects of different parameters on interaction between rock/fluid and fluid/fluid such as concentration and type of EOR agents, operational conditions such as salinity and temperature, and pressure of reservoir and injection conditions on the CEOR efficiencies? (v) How NASP can boost the oil recovery in real field projects? (vii) What are the main governing mechanisms of NASP in microscopic and macroscopic scales? Lastly, the authors will investigate the best scenario or method for guaranteeing the maximum oil recovery through NASP injection.

#### 2. The Mechanisms and Role of NASP in CEOR

The EOR project is hugely controlled by mobility of fluids in the pore spaces. Favorable mobility (M) is achieved through reducing the mobility ratio to less than 1.0. Unstable displacement front occurs if M > 1.0. In this case, the large contrast in oil and water viscosity (displacing phase) fingers into oil (displaced phase) leads to premature breakthroughs at production wells, decreasing oil production. To overcome the viscous fingering issue, a polymer is used to enhance the viscosity of the displacing phase to decrease the mobility of the displaced phase (Equation (1)):

$$\mathbf{M} = (\mathbf{K}_{rw}/\mathbf{K}_{ro}) \times (\mu_o/\mu_w) \tag{1}$$

where  $K_{rw}$  = water relative permeability,  $K_{ro}$  = oil relative permeability,  $\mu_w$  = water viscosity,  $\mu_o$  = oil viscosity. For microscopic sweeping, efficiency using AS (Alkaline Surfactant) has been utilized, in situ soap formation by alkaline flooding is not high enough to reduce IFT (Interfacial Tension) significantly [10]. The concept of using surfactant applies to washing surfaces of the oil reservoir rocks when these oils were trapped due to capillary pressure. ASP synergism is one of the successful CEORs in developing oil recovery in complex reservoir conditions. Moreover, it is cost effective in reservoirs that rely on gravity and imbibition in recovering the oil. Around 32 ASP field projects are surveyed in the literature [11]. Twenty-one field projects were reported in China followed by USA, India, Canada and Venezuela with 7, 2, 1 and 1 projects, respectively. Only one project was performed in an offshore reservoir, which was in Lagomar, Venezuela. Five-spot patterns were used in most of the ASP field projects [11]. Heavy alkylbenzene sulfonate was used in most of the projects. In these projects, pump working life and lifting system were damaged due to scale and corrosion. Due to scaling issues, weak alkali is widely used instead of strong alkali. The utilized surfactants were ORS-41HF, ORS-62, biosurfactant local Chinese surfactant product (OP10, KPS-1 and CY1), anionic surfactant (BES), (local petroleum sulfonate (YPS-3A), isobutanol, n-butanol, and isopropyl alcohol (cosurfactant). The main polymer used in an ASP slug was HPAM, 1275A, 3530S, and Pusher 700 [11]. Biopolymer (xanthan) was used only in one project [11].

Table 1 depicts a summary of previous ASP works while highlighting the role and mechanisms of each chemical alone and in hybrid for enhancing oil mobilization. To enhance the mobility and investigate the role of the injected NASP, the volumetric sweeping efficiency micromodel as a future new insight in EOR would have been a new recommendation for oil companies. A micromodel experiment (Figure 1) is a future planned model to investigate the mechanism of the fluid flow on porous media via flow visualization, fluid interactions, pore space geometry and heterogeneity effects. To carry out the test, the oil–wet glass micromodel would be saturated with oil, followed by the injection of the prepared hybrid nano-ASP solution. The micromodel is placed horizontally to avoid the gravity effect. During the tests, high resolution pictures will reveal the fluid distribution in the micromodel taken at various time intervals.



Figure 1. Future micromodel set up using NASP.

From the previous lab and experimental works, it is quite clear that, for mobilizing and improving the trapped oil effectively and efficiently, most of the EOR mechanisms such as mobility, IFT, and wettability should be controlled and activated. For this objective, the ASP synergism effect should be addressed extensively and optimum concentration of each chemical should be selected for boosting the oil recovery.

CEOR Type	Ref.	Chemical Name	Conc.	Porosity %	Permeability (md)	Lithology
		Na <sub>2</sub> CO <sub>3</sub>	1.0			
	[12]	NaOH	1.0	NA.	405-608	Sandstone
	-	Na <sub>4</sub> Si0 <sub>4</sub>	0.5			
	[13]	Na <sub>2</sub> CO <sub>3</sub>	0.85	25	70	Sandstone
	[2]	NaOH	0.5	NA.	1580	Sandstone
	[14]	NaOH	0.5	33.59	6000	Sandstone
	[15]	NaOH	0.2	NA	NA	Carbonate
	[2]	Na <sub>2</sub> CO <sub>3</sub>	NA	35.5	3200	Sandstone
ne	[16]	NaOH	0.5	38.7	NA	Sandstone
kali	[17]	NaOH	0.2	NA	NA	Sandstone
AI	[18]	NaOH	NA	15	119	Sandstone
	[19]	NaOH	4.85	20.6	25	Sandstone
	[20]	NaOH	0.15	16	NA	Sandstone
	[21]	NaOH	0.2	30	495–320	Sandstone
	[22]	NaOH	0.5	NA	2110	Sandstone
	[23]	NaOH	1.0	NA	NA	sandstone
	[24]	NaOH	2.0	19.7	93.64	Sandstone
	[24]	Na <sub>2</sub> CO <sub>3</sub>	2.0	19.6 176.25		Sandstone
	[25]	Na <sub>2</sub> C0 <sub>3</sub>	1.20	35	3850	Sandstone
	[26]	Cationic C <sub>12</sub> TAB	NA	45–50	2–5	Carbonate
	[27]	SDS	1000	52.2	250	Carbonate
	[25]	OPIO and CY1	NA	35	3850	Sandstone
	[28]	Anionic surfactant	NA	29.06	19.72	Carbonate
	[29]	Nonionic surfactants	NA	NA	20.89	Carbonate
	[30]	Anionic surfactant	NA	3–5	NA	Carbonate
	[31]	nonionic ethoxy alcohol	3000-4000	3–5	NA	Carbonate
ant	[32]	Anionic (GAC) surfactants	NA	NA	NA	Carbonate
fact	[33]	Nonionic (POA)	750	15.4	56	Carbonate
Sur	[34]	Nonionic ethoxy alcohol	50-3500	NA	NA	Carbonate
	[16]	SDS	1000	38.6	212	Sandstone
	[35]	SDBS	250	37	284	Sandstone
	[36]	SLPS	1000	38	NA	Sandstone
	[37]	SDS	3000	NA	NA	Glass bed
	[38]	XD	1000	NA	NA	Sandstone
	[39]	SDBS	2000	25	NA	Sandstone
	[13]	SDS	NA	23–29	50–94	Sandstone

 Table 1. Summary of previous experimental and field ASP works alone and in synergy.

CEOR Type	Ref.	Chemical Name	Conc.	Porosity %	Permeability (md)	Lithology
	[10]	PAM	3200	NA	405 to 608	Sandstone
ner	[12]	Xanthan gum	1540	NA	405 to 608	Sandstone
	[36]	(HPAM)	1000	37.5	3780	Sandstone
	[40]	(Gum Arabic/Poly acrid	NA	NA	NA	Sandstone
	[41]	HPAM	1100	21.6	420	Sandstone
oly	[42]	TVP	2000	NA	NA	Sandstone
8	[43]	HPAM	1800	NA	NA	Sandstone
	[44]	PAM	500	>39	100-60	Sandstone
	[16]	PHPAM	1500	37.3	218	Sandstone
	[45]	HPAM	1200	15.2	23.34	Sandstone
	[46]	Xylene + NaOH	5000 + 10,000	NA	NA	Carbonate
	[47]	$IOS + Na_2CO_3$	(200–10,000) + 5000	37	2400	Micromodel
	[48]	$Na_2CO_3$ + alkyl ether sulfates	1500 + 50	NA	NA	NA
ant		Na <sub>2</sub> CO <sub>3</sub> + XD 10,000 + 1000 NA		NA	NA	Sandstone
facti	[38]	Na <sub>2</sub> CO <sub>3</sub> + SDS	10,000 + 10,000	NA	NA	Sandstone
Sur	[49]	$(IOS) + NaOH + Na_4Si0_4$	NA	NA	NA	Sandstone
line	[50]	NaOH + SLPS	3000 + 300	44.7	2131	
llkal		NaOH + SLPS	8000 + 1000	43.50	1994	Sandstone
A		NaOH + SLPS	10,000 + 1000	44.21	2016	
	[13]	$SDS + Na_2CO_3$	1000 + 8500	25	70	Sandstone
	[51]	Na <sub>2</sub> CO <sub>3</sub> + sodium alkane sulfonate	(1000–15,000) + 1000	41-45	790–19,220	Sandstone
	[52]	Na <sub>2</sub> CO <sub>3</sub> + anionic PAM	NA	15.5	21	Sandstone
	[53]	Na <sub>2</sub> CO <sub>3</sub> + Pusher 1000E	8000 + 600	29	1400	Sandstone
	[54]	NaOH + Alcoflood 1275A	10,000 + 1000	20	200	Sandstone
		NaOH + HPAM	10,000 + 1000	38.92	2350	
ner	[55]	Ethylenediamine + HPAM	10,000 + 1000	39.41	2230	Sandstone
olyı		Na <sub>2</sub> CO <sub>3</sub> + HPAM	10,000 + 1000	40.33	2420	
ne p	[56]	Na <sub>2</sub> CO <sub>3</sub> + anionic PAM	NA	15.5	21	Carbonate
kaliı	[57]	$(NaOH + Na_2CO_3) + HPAM$	(4000 + 2000) + 250	34.43	4800	Sandstone
All	[57]	HPAM + $(NaOH + Na_2CO_3)$	1000 + (1000 + 2000)	35.25	6400	Sandstone
	[52]	Na <sub>2</sub> CO <sub>3</sub> + Alcoflood 1175	10,000 + 800	29	1400	Sandstone
	[58]	Na <sub>2</sub> CO <sub>3</sub> + PAM	10,000 + 1500	31	840.9	Sandstone
	[25]	Na <sub>2</sub> C0 <sub>3</sub> + OP-10	1200 + 10,000	35	3850	Sandstone
	[59]	Na2CO3 + HPAM         20,000 + 1000			2063	Carbonate

CEOR Type	Ref.	Chemical Name	Conc.	Porosity %	Permeability (md)	Lithology
	[60]	alkyl ether sulfates + Witco petroleum sulfonate	1000 + 1000	12	5.9	Carbonate
	[61]	Amphoteric + PAM	2500 + 1400	29.1	3442	Sandstone
	[62]	PAM + SDS	1000 + 2200	21	66	Sandstone
	[16]	SDS + PHPAM	1000 + 2000	36.8	1224	Sandstone
	[63]	bio-surfactant and biopolymer	1001 + 5000	17	400	Sandstone
mer	[61]	PS + PAM	2000 + 2000	21	115	Sandstone
oly	[39]	SDBS + HPAM	2000 + 2000	25	NA	Sandstone
unt p		PAM + SDS	2800 + 1000			
facta	[64]	PAM + SDS	2800 + 2000	NA	NA	Glass mi- cromodel
Surf	-	PAM + SDS	2800 + 3000			cromoder
	[61]	(Amphoteric +anionic) + PAM	1200 + 1500	15	110	Sandstone
	[36]	HPAM + SDS	1000 + 1000	38	1410	Sandstone
	[45]	anionic surfactant + HPAM	1200 + 1200	15.2	23.34	Sandstone
	[43]	SLPS + HPAM	4000 + 1800	NA	1500	Sandstone
	[65]	KPS + HPAM	3000 + 115	14.7	5.08	Sandstone
	[43]	SLPS + (HPAM)	4000 + 1800	NA	1500	Sandstone
		NaOH + SDS + PHPAM	5000 + 1000 + 2500			
	[60]	NaOH + SDS + PHPAM	5000 + 2000 + 2500	NA	NA	Sandstone
	-	NaOH + SDS + PHPAM	5000 + 3000 + 2500			
	[66]	Amphoteric Petrostep B-100 + Pusher 700E + Na <sub>2</sub> CO <sub>3</sub>	4000 + 1200 + 20,000	8–43	1–600	Carbonate
SP)	[67]	Na <sub>2</sub> CO <sub>3</sub> + SDS+ PAM	10,000 + 1000 + 800	NA	NA	Sandstone
er (A		NaOH + SDS + PHPAM	5000 + 1000 + 1500			
yme	[16]	NaOH + SDS + PHPAM	7000 + 1000 + 1500	38.7	NA	Sandstone
pol	-	NaOH + SDS + PHPAM	10,000 + 1000 + 1500			
tant		NaOH + SDS + PHPAM	5000 + 1000 + 1500			
rfac	[16]	NaOH + SDS + PHPAM	5000 + 1000 + 2000	38.7	NA	Sandstone
e su	-	NaOH + SDS + PHPAM	5000 + 1000 + 2500			
ulkalin	[68]	Na <sub>2</sub> CO <sub>3</sub> + Petrostep B-100 + Alcoflood1175A	12500 + 1000 + 1475	18	845	Carbonate
V	[69]	Diethylene glycol butyl ether + alcoflood-2545 + NaBO <sub>2</sub>	3000 + 10,000 + 10,000	17.7	239	Sandstone
	[70]	HAPAM + NaOH + heavy alkylbenzene sulfonate	1000 + 1200 + 3000	NA	252	Sandstone
	[71]	Na <sub>2</sub> CO <sub>3</sub> + (anionic BES and lignosulfonate PS) + PAM	12,000 + 3000 + 1700	NA	NA	Sandstone

CEOR Type	Ref.	Chemie	cal Name	Conc. Porosity Permeability Lit % (md)		Lithology			
CEOR Type	Ref.	Work Type	Oil Improvement %	Remark					
	[12]			17.2					
		Experimental	9.42	Na <sub>2</sub> CO <sub>3</sub> is more effective for oil increment					
			8.91	-					
	[13]	Experimental	4.4	Due to soap formatio	n, Interfacial tens phase redu	sion between olei 1ced	c and aqueous		
	[2]	Experimental	12.4	Low salinity leads to	O/W emulsions emulsions h	if the salinity is a appen	bove 0.7 W/O		
	[14]	Experimental	13.33	IFT reduction d	ue to soap forma	tion improves oil	recovery		
	[15]	Experimental	NA	Alkaline flooding compared to light cru	g is more applica 1de oil due to a h medium cru	ble for medium c igher ratio of soaj de oil	rude oil as 5 formation in		
e	[2]	Experimental	14	Alkaline is also a	applicable and ca horizontal	n accelerate oil re wells	covery in		
alin	[16]	Experimental	13.88	Strong base (NaC	DH) alkaline injeo	ction enhanced oi	l recovery		
Alk	[17]	Experimental	NA	Higher oil rec	overy due to in s	itu. Emulsion for	mation		
	[18]	Experimental	2	additional oil	guaranteed by c	hanging the wett	ability		
	[19] Field			the amount of IFT reduction determines the success of alkali job					
	[20]	Field	2	Changing in rock surface wettability directly affects oil recovery					
-	[21]	Field	5 to 7	Formation of the emulsion by alkaline improves volumetric sweep efficiency					
	[22]	Experimental	12.9	The oil displacement experiment proved that oil recovery is enhanced by using alkaline injection					
	[23]	Experimental	<1	Orthosilicate was ve	ry successful at s increasing oil 1	stopping water ch ecovery	anneling and		
	[24]	Experimental	2.52 3.67	NaOl	H is more effectiv	ve than Na <sub>2</sub> CO <sub>3</sub>			
	[25]	Field	9.13	Ultra	-low IFT after al	kaline flooding			
	[26]	Experimental	20	changing rock surfac	e wettability due the injection	e to the sulfate tha fluid	it is present in		
	[27]	Experimental	9	Oil recovery affected	by the type and used in the for	concentration of rmation	the surfactant		
	[25]	Field	11.64	Higher amount	of IFT reduction	leads to more oil	recovery		
	[28]	Experimental	30	Optimum surfacta	nt concentration	is related with br	ine salinity		
actant	[29]	Field	NA.	About 58,000 bbl of oil is produced after using Nonionic surfactan over only three months					
Surf	[30]	Experimental	NA	The performance of anionic surfactants was more effective than nonionic surfactants					
	[31]	Experimental	15.0	to optimize surfactar a	nt performance in re the important	njection rate, conc parameters	and volume		
	[32]	Experimental	NA	I	FT significantly of	diminished			
	[33]	Experimental	10.4	Nonionic sur	factant outperfor	med cationic surf	actant		
	[34]	Experimental	NA	surfactants dec	reased IFT and c	hanged the conta	ct angle		

CEOR Type	Ref.	Chemical	Name	Conc.	Porosity %	Permeability (md)	Lithology		
	[16]	Experimental	17.96		IFT decreased n	narginally			
	[35]	Experimental	2.1	Due to surfactant degradation, the oil recovery was low					
	[36]	Experimental	4	Increase in capillary number yields more oil recovery					
ant	[37]	Experimental	NA	IFT reduced from 19.59 to 2.82 mN/m					
urfact	[38]	Experimental	11.5	At lower concentratio	on, a novel XD y can be compared	vielded a good oil 1 with SDS	recovery that		
U)	[39]	Experimental	4.6	Compared to SP floo	oding, oil recove was redu	ry by using surfac ced	tant flooding		
	[13]	Experimental	7.1	Adsorption phenome	ena indicated that sandstone for	at SDS was a suita mation	ble choice for		
	[12]	Experimental	11 10.5	Pol	ymer type selec	tion is critical			
	[36]	Experimental	10.7	Increasing the vis	cosity of water l sweep effic	oy HPAM improv iency	es vertical		
	[40]	Experimental	5.2	Core flood test indicat other polyn	tes that this type ner types due to	of polymer is less less oil improven	effective than nent		
ST.	[41]	Field	9.8	Higher molecular weight improves thermal stability					
Polyme	[42]	Experimental	13.5	Temperature affects polymer performance					
	[ (0]		6.3	PPG is more effective in higher and lower permeability zones					
	[43]	Experimental –	13.4	compared to conventional polymer (HPAM)					
	[44]	Field	7	Earlier injection of polymer is more profitable					
	[16]	Experimental	16.12	High viscos	sity of polymer l macroscopic dis	eads to an increas placement	e in		
	[45]	Experimental	8.80	From the results, it c reach	an be indicated to the unrecove	that polymer is us erable oil zones	sed mostly to		
	[46]	Field	10–15	Alkaline-surfactant floor of the high residu	ooding offers a j 1al oil that was r	potential scheme t not recovered by v	o recover part vaterfront		
	[47]	Experimental	NA	Emulsifica	tion of heavy oi	l by AS was effect	ive		
	[48]	Experimental	NA	For mobilizing hea	avy oil, AS flood	ling is a very suita	ble choice		
t	[20]	Europeine en tel	14.58	In eiter open her ell	l	unt un der eine IET eine			
ıctar	[38]	Experimental –	10.42	— In situ soap by all	kall and surfacta	int reduces IF I sig	snincantiy		
e surfa	[49]	Field	NA	Alkaline is not able to reaches mir	o mobilize oil alc nimum value an	one, when surfacta d oil easily mobili	ant added IFT zed		
alin			12.10						
Alk	[50]	 Experimental	15.80	Surfactant and soap (in situ) surfactant formation					
			18.63	emciently reduces IF I					
	[13]	Experimental	18	As shown in adsorg rec	ption phenomer ducing surfactar	na, alkali plays a n nt adsorption	najor role in		
	[51]	Experimental	10.5	Surfactan	t reduces the all	kaline consumptio	n		

CEOR Type	Ref.	Chemical Name		Conc. Porosity Permeability Lithology (md)				
	[52]	Field	NA	AP synergy effect was efficient for improving EOR mechanisms				
	[53]	Field	21.1	AP was sufficient to improve oil recovery				
	[54]	Field	17	Binary system of A and K performance is more significant than usir each of the chemicals alone				
			21.02					
	[55]	Experimental	25.21	In AP flooding, alkaline selection plays a critical role in oil recovery improvement				
ner			18.12					
aline polyı	[56]	Field	26.4	Soap formation by Na <sub>2</sub> CO <sub>3</sub> and viscosity improvement by anionic polymer yielded higher recovery				
		E	18.58					
Alka	[57]	Experimental –	27.60	Conc. of polymer influences oil recovery				
·		E	16.56					
	[57]	Experimental —	27.39	Conc. of Alkaline influences oil recovery				
	[52]	Field	21.1	67% OOIP was recovered by AP				
	[58]	Experimental	22.8	Polymer solution should be injected at a good speed				
	[25]	Field	18.12	alkali cannot to the oil region without polymer				
	[59]	Experimental	1.98	Mobility control improved				
	[60]	Experimental	12.0	Using two surfactants was more effective				
	[61]	Field	16.3	Using surfactant with polymer yield extra oil recovery				
	[62]	Experimental	17.25	Temperature and initial oil saturation affects oil recovery				
	[16]	Experimental	20.99	Better mobility control is obtained by using polymer with surfactant				
	[63]	Experimental	15.94	The binary system demonstrated high interfacial activity with IFT min below 0.01 mN/m				
	[61]	Field	13.8	Synergism of polymer and surfactant further improves oil recovery				
: (SP)	[39]	Experimental	20	Oil recovery after using dual chemicals (S and P) was higher than the total oil that is produced by using S and P alone				
imei			41					
Poly	[64]	Experimental	41.4	CMC of SDS is 0.21 means that higher concentrations of CMC have a marginally effect on oil recovery				
ant ]			42					
urfact	[61]	Field	14.5	Polymer and surfactant synergism developed by choosing the optimum conc. of each				
S	[36]	Experimental	13.7	Without polymer injection surfactant cannot go through unsweep zones				
	[45]	Experimental	11.29	Anionic surfactant for sandstone reservoir is very effective				
	[43]	Experimental	13.6	Polymer and surfactant synergistic yields higher oil displacement				
	[65]	Experimental	23.96	Polymer controls mobility control and surfactant reduces IFT				
	[43]	Experimental	22.4	SLPS improves displacement efficiency and (HPAM + PPG) improves sweep efficiency				

CEOR Type	Ref.	Chemica	l Name	Conc.	Porosity %	Permeability (md)	Lithology		
			23.69						
	[60]	Experimental	27.18	— Increase in surfactant conc. leads to oil recovery enhancement					
		_	28.72						
	[66]	Experimental	45	An alkaline surfactan in recovering c	t polymer form oil than surfacta	ulation was substa nt or polymer surf	ntially better actant		
ner (ASP)	[67]	Experimental	7.4	A, S and P synergism yielded higher oil recovery. Alkaline redu surfactant adsorption. Surfactant reduces alkaline consumption polymer increases the viscosity of water. These three functions pl great role in recovery enhancement					
nt Polyı	[16]		23.69	Effect of different alkaline concentration in ASP slug yields differer oil recovery, indicating that optimum concentration of alkaline					
		Experimental	24.08						
acta			24.91	should be guaranteed					
surf			23.69						
ine	[16]	Experimental	23.5	Optimum concentration of polymer is required during ASI for higher oil recovery	ASP injection				
lkal		_	24.2		ior ingrier on i	lecovery			
A	[68]	Field	28.1	ASP syner	gy effect makes	the process efficies	nt		
	[69]	Field	10–28	Pore scale displacement efficiency improved due to synergy of three chemicals					
	[70]	Field	>25	NaOH and heavy alkylbenzene sulfonate reduces IFT dramatically and polymer pushes the heavy oil					
	[71]	Experimental	15.5	Present the co-surfactant in the ASP slug is critical in releasing th trapped oil in the porous part of the reservoir rock					

Different kind of ASP flooding in different reservoir characteristics, close up percentage of oil improvement. From this table, it is obvious that ASP is one of the promising EOR applications due to its dual efficiency effect, alkaline and surfactant microscopic efficiency, and polymer progresses volumetric sweep. Reservoir fluid and rock property play a vital role for ASP selection, and, for achieving highest oil recovery, suitable ASP type and concentration should be used. For sandstone formation, the convenient surfactant type was used in ASP is SDS. CTAB is mostly used for carbonate due to its surface charge. Lith = Lithology; P. = Porosity; Pb. = Permeability; Sst = Sandstone Carbo. = Carbonate; Qz = Quartz; SDS = sodium dodecyl sulfate; GAC = Guerbet alkoxy carboxylate; POA = poly-oxyethylene alcohol; PAM = Polyacrylamide: HPAM = hydrolized polyacrylamide; C<sub>12</sub>TAB = Dodecyltrimethylammonium (bromide); SDBS = Sodium Dodecylbenzene Sulfonate Surfactant; KPS = Potassium persulfate; XD = xylitoldehydrogenase; TVP = thermo-viscosifying polymer; IOS = internal olefin sulfonate; PS = Pulmonary surfactant; SLPS = surfactant like peptides.

# 3. Natural Surfactants

Natural surfactants mostly derived from the seeds; like chemical surfactants, natural surfactants may be ionic, polymeric, nonionic or amphoteric (Table 2). The critical micelle concentration (CMC) value of synthesized natural surfactant ranges between 9–10 mM, yielding an IFT between 0.075 to 0.125 mNm<sup>-1</sup>. Natural surfactant can also reduce the contact angle efficiently besides IFT reduction. Several extraction methods are explained for synthesizing natural surfactant, but the main methods were spray dryer, soxhlet extraction, methanolic extraction, and maceration process. Different natural surfactant types versus minimum interfacial tension value are depicted in Figure 2. However, Ref. [72] explored the fact that honeycomb micro-porous structures are effective in separating water from oil, hence it may be very significant in diminishing water–oil IFT.

The previous work results (Table 2) declared that, in addition to the commercial surfactants (Table 1), natural surfactants are effective with decreasing IFT, wettability alteration and adsorption on the solid surface. Nowadays, researchers are focusing on applying this type of surfactant because of some advantages and reasonable features such as cost effectiveness, less toxicity, more stability and effectiveness at high pressure and

temperature and more biodegradabilities as compared to commercial surfactants (Table 1). These kinds of surfactants can increase oil recovery by about 5–40% of OIIP.

Table 2. Summary of natural surfactant types and their properties.

Ref.	Name	СМС	Туре	IFT From-to mN/m	Contact Angle From-To	Oil Recovery Improvement %	Properties
[73]	Reetha Extract	2.3	Natural non-ionic	18.6 to 7.02	NA	6.8	Applicability of new surfactant and increase oil recovery from 18.5 to 25.3
[74]	Mulberry leaves extract	2.6	Natural cationic	44 to 17.9	62.5° to 42.5	7	Suitable for carbonate rock
[75]	Matricaria chamomilla extract	0.05	Natural Nonionic	30.63 to 12.53	NA	NA	Good IFT reduction ability
[76]	Cordia Myxa plant	0.06	Natural	33 to 16.24	NA	27	Good adsorption
[77]	Mahua oil	NA	NA	$10^{-2}$	NA	20	Applicable for sandstone reservoir
[78]	Seidlitzia rosmarinus extract	0.08	Cationic	32 to 9	NA	NA	The reduced IFT is not as low for EOR application
[79]	Jatropha oil-based	NA	Nonionic	0.917	NA	25	Good surface activity
[80]	Henna extract	0.02	Cationic	43.9 to 3.05	66 to 37	7	Good wetting ability
[81]	Olive leaf extract	1.95	Natural cationic	36.5 to 14	NA	NA	Good adsorption
[81]	Spistan leaf Extract	2.1	Natural cationic	36.5 to 20.15	NA	NA	good associative and interfacial properties
[81]	Prosopi leaf Extract	2.3	Natural cationic	36.5 to 15.1	NA	NA	Good adsorption





# 4. Potential of NASP Synergism

To increase the potential of EOR, the optimum chemical solution is achieved at large injection volumes through injecting alkaline, polymer and surfactant (Figure 3). Oil improvement through ASP flooding has been reported previously. The principle of this method is the reaction between alkali and organic to create petroleum soaps. These petroleum soaps will interact with surfactants to reduce the IFT to minimum value ( $10^{-4}$  mN/m). In addition, the polymer is used to reduce the viscosity ratio of oil/water interface. Reduction

of IFT and oil viscosity significantly improve vertical and displacement efficiency. ASP flooding is used for heavy oil reservoirs [25]. Recently, nanoparticle is mixed with the chemicals above to reduce the cost of these chemicals, modify the wettability, minimize oil-water IFT and boost oil recovery efficiency. Table 3 examines the types of process efficiencies for each of the methods used in the article, and predicts the amount of efficiency by NASP:

$$Ero = E_{do} E_a E_v \cdot \frac{So Vp}{Bo}$$
(2)

where  $E_{do}$  is the microscopic displacement efficiency increased by using the optimum surfactant and alkaline type and concentration, *Vp* is the permeability variation and *So* is the oil saturation.  $E_a$  and  $E_v$  are displacement efficiencies of areal and vertical, developed by using the appropriate polymer.



**Figure 3.** ASP chemical flooding sequence for enhancing oil recovery. ASP EOR injection is shown in sequence at the beginning, the preflush is injected then followed by oil bank; after that, nano-alkaline-surfactant is injected to decrease the IFT followed by a polymer to control the mobility via increasing the viscosity; finally, water drive is used to push the solutions.

CEOR Type	Oil Recovery %	Basic Principle
Nano	5–23	Improvement in sweep and displacement
Alkaline	2–5	Improvement in displacement
Polymer	2–10	Improvement in sweep
Surfactant	5–15	Improvement in displacement
SP	5–20	Improvement in sweep and displacement
AP	5–18	Improvement in sweep and displacement
ASP	5–25	Improvement in sweep and displacement
Nano-polymer	4–20	Improvement in sweep and displacement
Nano-surfactant	5–20	Improvement in sweep and displacement
NSP	8–22	Improvement in sweep and displacement
NASP	>25 (predicted by our study)	Improvement in sweep and displacement

## 5. NASP Prediction Technical Characteristics

The NASP synergism limits the polymer adsorption and high alkali consumption [82]. Figure 4 illustrates the main reasons for NASP interaction. The predicted technical properties of NASP EOR compared to single element flooding are summarized as follows:

- The amount of surfactant is significantly lowered in NASP system;
- Strong or a weak base alkali is used in the ASP synergy system;
- NASP significantly increases oil recovery since it has physical and chemical (dual) effects;
- It is forecasted that, when the four-element composites (N, A, S, and P) are used together, the IFT rapidly decreases to 0.001 or lower.



Figure 4. NASP interaction improved mechanisms.

#### 6. Screening the Reservoir Rock Properties

Screening criteria can determine the suitable EOR process for the target reservoir rocks and control the cost issue. Sheng [60] summarized the significant parameters of ASP process, EOR, permeability, clay contents, reservoir temperature, pressure, divalent contents, formation water salinity and oil viscosity.

Due to high anionic surfactant adsorption on carbonate, nearly all the chemical (CEOR) processes were conducted on sandstone reservoir rocks. The presence of anhydrate mineral in carbonate formations caused severe alkaline consumption [83]. On the other hand, clays in sandstone reservoirs caused surfactant adsorption. Thus, clay percentage should be lowered for effective and successful ASP flooding. The permeability is another criterion and very critical to polymer injection in the ASP project since a polymer is not able to flow through tight or low permeable reservoirs.

For alkali, the crude oil composition is a very critical point, while, for polymers, it is not significant [83]. The viscosity of oil should be >35 cP for AS projects. The oil viscosity in Chinese fields projects is from 10–70 cP. According to some authors, it is preferred to apply polymer EOR in reservoirs with viscosity of 2000 cP [84].

ASP projects are more convenient in low salinity reservoirs 10,000 ppm of total salinity [85]. The preferable reservoir temperature is 93 °C for ASP, while the average reservoir temperature for AS field projects was 27 °C, even up to 80 °C, was documented [85]. Recently, scholars have been thinking about using optimum chemicals, in particular polymers, to withstand high salinity and temperature [85].

# 7. ASP/EOR Process Challenges

Even though a chemical ASP process is the most effective chemical process for decreasing water cut and oil enhancement, tight oil produced in water emulsion creates huge problems [86]. In addition, several problems and limitations are associated with offshore ASP/EOR applications [87]. Large chemical volumes that are transported to remote sites, and less space availability, lead to difficulty in operation [86]. Extra treatment is needed for the produced fluid containing alkaline, polymer and surfactant. This tight emulsion formation leads to difficulty and limitation in the separation process [86]. Literature revealed that this chemical process works more efficiently in low salinity water reservoirs [87]. Nevertheless, the source of water injection is from the seawater; therefore, alternative chemicals may be needed. Divalent cations in the system are the main source of scaling.

## 7.1. Operational Difficulties

Like any CEOR injection, ASP are associated with many operational problems such as corrosion, scaling, pump failures, polymer degradation, and low injectivity [82]. In addition, this process is complex in design and needs water and oil analyzing. Moreover, due to a large volume of chemicals, the cost of this process should be analyzed effectively. Finally, this EOR flooding type is not favorable for hot reservoirs or those with saline water [82].

#### 7.1.1. Scaling Issues during ASP Flooding

Calcium and magnesium reaction with the injected alkali leads to a scaling issue. This effect is regarded as one of the ASP limitations since this reaction leads to extreme surfactant precipitation and alkali consumption [88,89]. Several publications reported scaling issues during ASP injection into the reservoir [90–93]. Scales may originate from the alkalis and carbonate mineral's reaction. According to the literature, silicate scale formation is a very sophisticated mechanism because the problems associated with silicate are poorly understood. In Chinese oil fields, scaling issues have been observed and reported [93].

#### 7.1.2. Surfactant Precipitation

Divalent cationic existences in hard brines cause surfactant precipitation as illustrated in Equation (3):

$$2R^- + M^{2+} \to MR_2 \tag{3}$$

where  $MR_2$  is the surfactant divalent cation, and R the anionic surfactant. Different factors like temperature, alcohol and salt concentration are responsible for anionic surfactants' precipitation [94]. In most of the cases, the presence of oil reduces surfactant precipitation efficiently since oil competes for surfactant. Ethoxylate (EO) helps surfactant to resist divalent cations. At lower hardness, monovalent cation is formed from the reaction of multivalent cation with the anionic surfactant [94].

#### 8. Prospects and Future Developments of ASP/CEOR

Based on this review paper, the following conclusions and recommendations can be proposed for this study:

- ASP limitations could be due to alkaline since alkaline reduces polymer viscosity. Thus, a big question is: can SP work more effectively than ASP?
- Due to the carbonate rock complexity, most of the nano-EOR flooding has to be performed on sandstone rocks. Further studies should be implemented for understanding the effect of oil recovery on carbonate rocks;

- More sophisticated and advanced tools should be used to accurately examine the role of NASP in changing the wettability and IFT;
- Due to the lack of economic data in the research papers, more economic study should be implemented to evaluate the economic performance of NASP in accelerating oil recovery;
- HS and HT could limit NASP to work effectively in maximizing oil recovery. This
  is why a more effective nano, surfactant and polymer should be developed to limit
  this issue.

More research is needed to evaluate the performance of NASP in sandstone and carbonate reservoirs.

# 9. NASP Performance Anticipation in Changing the Wettability and IFT

After reviewing and evaluating ASP lab and field projects, it is forecasted that NASP could modify wettability and IFT effectively more than any other previous chemical methods due to the synergism effect of ASN (Alkaline Surfactant Nano), and it may stabilize the polymer solution excellently due to the NP synergism effect. Based on the above points, ultimate oil recovery could be guaranteed by implementing NASP. IFT and contact angle are the main parameters of any EOR type since it is related to the capillary number modification. Due to accuracy and ease of use, pendant drop is considered as one of the main methods to calculate IFT and contact angle. IFT study will be implemented by introducing a drop into a bulk phase under the desired P and T. For contact angle measurement, the drop is completed on a plane solid sample. Pictures captured by a digital camera connected to a computer show the shape of the drop and allow for solving the Laplace equation contact angle and IFT calculation. Figure 5 illustrates IFT and contact angle measurement by using pendant drop.



Figure 5. IFT and contact angle measurement by using pendant drop (oil drop).

# **10. Core Flooding**

For recovery measurement, a dynamic test will be prepared by core-flooding. Different core plugs are used with injecting best chemical, nanofluid and hybrid nanochemical solutions under the reservoir condition. For this purpose, a core sample should undergo several procedures to be prepared and aged. After aging, the brine solution is injected, followed by the injection of a hybrid Nano-ASP solution to study oil recovery from the carbonate rock. Then, the values of oil production are recorded vs. time. Finally, oil recovery is plotted vs. pore volume. This review paper forecasted that oil recovery by NASP could be more than 25% due to the improved mechanisms that have been discussed in the other sections. Figure 6 illustrates NASP core–flood procedure.



Figure 6. Core–flood procedure.

# 11. Future Design, Materials and Features of NASP Process

#### 11.1. Nano-EOR

Nanoparticles are wide classes of material substances, with sizes between 1–100 nm. Nowadays, the oil and gas industry has attracted much consideration on applications of nanoparticles (NPs). NPs have become widely used due to having unique optical, magnetic and electric features. Mixing nanoparticles with other substance phases is called nanocomposites (NCs). NPs within different dispersion media can be easily transported through the porous media and reach the oil bank due to their smaller sizes, less than micron-sized rock pores. Consequently, NCs can be used to decrease ASP adsorption with the rock surface, altering the wettability of the rock, reducing the interfacial tension (IFT)

and improving oil displacement and recovery (Figure 7). The surface area-to-volume ratio of nanoparticles is too large, where a small concentration of them is needed to induce EOR injection fluids. Combining nanoparticles with the natural polymers develop polymeric nanofluids, thus the resulted NPs would have a better stability, mobility of injection fluids and sweep efficiency.



Figure 7. IFT reduction and wettability alteration by nanoparticles.

Figure 7 highlights that the nanoparticles can alter the wettability and reduce oil water IFT. The mechanism of wettability alteration by nanoparticles is to build a wedge film on the oil droplet and the rock surface. The nano size particles re-arrange themselves between the rock and oil droplet, leading to oil separation and thus altering the wettability from hydrophobicity to hydrophilicity, and decreasing the excessive surfactant adsorption. Moreover, disjoining pressure is regarded as one of the nanoparticle mechanisms in EOR since it responsible for changing the oil wet surface to water wet. This mechanism is highly affected by nanoparticle type and concentration. Different nanoparticle types play different roles in the EOR mechanism process (Table 4).

Table 4. Role of different nanoparticles in EOR mechanisms.

Nanoparticle	Nano-Composites	EOR Mechanisms
$SnO_2$ , $ZrO_2$ , Carbon nanoparticles $CTAB + Al_2O_3$		Wettability alteration by disjoining pressure
SiO <sub>2</sub> NiO + SiO <sub>2</sub>		Change wettability of oil by disjoining pressure
ZnO	$SDS + ZrO_2$	Decreasing the contact to water wet by disjoining pressure
Al <sub>2</sub> O <sub>3</sub>	$SiO_2 + PAM$	Wettability alteration by disjoining pressure
Fe, SiO <sub>2</sub> , GO, TiO <sub>2</sub>	ZrO <sub>2</sub> , NiO	Reduce interfacial tension
Al <sub>2</sub> O <sub>3</sub> , CuO, Fe <sub>2</sub> O <sub>3</sub>	$SDS + Al_2O_3$	Reduce the viscosity of crude
MgO	CuO/TiO <sub>2</sub> + PAM	Optimized permeability

## 11.2. Summary of Nano (NASP) EOR Flooding

Nanoparticles are very effective in changing the wettability and contact angle. Recently, nanoparticles were mixed with surfactant, polymer and SP to further improve oil recovery. The shape, size, dispersion media, nature and concentraion of nanoparticle will govern the most suitable and effective nanoparticles for achieving the best EOR mechanisms (Table 4). The main advantages of using nanoparticles are their large surface areas with spherical nanoparticles being more effective than any other nanoparticle shapes.

The main parameters that control the nanoparticle shape is the temperature, pH and time. In addition, nanoparticles play an astonishing role in improving the oil recovery since smaller nanoparticle size leads to lower IFT and contact angle (Figure 7). Furthermore, lab works hypothesized that optimum concentration should be guaranteed for any EOR application; otherwise, nanoparticles will agglomerate, leading to lower recovery efficiency. Regarding the dispersion media, our review paper finds out that different oil recovery is accomplished through dispersing nanoparticles into different dispersion media. However, Rajabi et al. used the wettability modifier: nanoparticles, surfactant and alkaline, but the highest percent of oil recovery was obtained by nano-surfactant rather than by adding alkaline [95]. The latter did not cause any positive impact on EOR. Furthermore, the oil improvement, using different kinds of nanoparticles, nano-polymers, nano-surfactants and nano-surfactant-polymers, efficiently decreases contact angles and IFT (Table 5), despite the fact that heterogeneity of sedimentary rocks could influence the quantity of oil improvement. The sedimentary rocks, especially carbonate rocks, characterized intensive lithological changes along micrometer-sized scales in both subsurface [96] and near-surface conditions [97]. This heterogeneity in enhanced oil recovery is the main cause behind the failure of oil recovery in the field scale. Therefore, the new model or design (NASP) for future experimental work should be achieved with detailed work on reservoir characteristics, including mineralogy and, of course, by detailed observations (both optical microscope and SEM).

**Table 5.** Summary of nano, nano-surfactant, nano-polymer and nano-SP flooding. It is concluded that a combination of nanoparticle and nanocomposites with conventional CEOR methods improves the synergism effect. As shown in the summary table, nanoparticles are used to support alkaline and surfactant in IFT reduction and wettability modifications (microscopic improvement). In addition, it is used to lower surfactant costs through controlling surfactant adsorption on the rock surface. In the case of polymers, nanoparticles improve the mobility of the polymeric solution, resulting in better oil sweep efficiency and reducing breakthrough time (macroscopic improvement). Lith = Lithology; Sst = Sandstone; Carbo. = Carbonate; Qz = Quartz.

Def	Nana Truna	T ::1.	Contact	t Angle	IF	Т	Oil Im-	<b>Domovi</b>
Kel.	Nano Type	Litn.	Before	After	Before	After	provement %	Kemark
	SiO <sub>2</sub>		131	38.82	19.2	17.5	2	
[98]	TiO <sub>2</sub>	Qz	131	21.64	19.2	NA	11	Different nanoparticles' type and size
-	Al <sub>2</sub> O <sub>3</sub>		131	28.6	19.2	12.8	8	have unicient performances
[99]	SiO <sub>2</sub>	Sst	51	30.5	21	20.3	10.1	Due to NP adsorption, the wettability altered from oil to water wet
[100]	SiO <sub>2</sub>	Sst	NA.	NA	NA.	NA.	4.29	Wedge film creation by nanoparticles
[101]	SiO <sub>2</sub>	Sst	122	16	13.62	10.69	23.5	Increase in capillary number due to SIO <sub>2</sub>
[102]	graphene nanosheets	Sst	NA.	NA.	NA.	NA.	6.7–15.2	Size of nanoparticle plays a great role in EOR
[103]	SiO <sub>2</sub> /TiO <sub>2</sub>	Set	154	23	NIA	NIA	NIA	Spherical shape of nanoparticle
[103] =	Al <sub>2</sub> O <sub>3</sub> /TiO <sub>2</sub>	Sst	154	24	$ \mathbf{N}\mathbf{A}$ .	NA.	1NA.	improves uniformity

	Nano Type	Lith.	Contact Angle		IFT		Oil Im-	
Ref.			Before	After	Before	After	provement %	Remark
[104]	HLP	– Sst	135.5	95	26.3	1.75	32.2	NPS yields higher oil recovery without
[104]	NWP		135.5	82	26.3	2.55	28.57	creating any damage to the formation
[105]	NiO/SiO <sub>2</sub> NCs	Carb.	174	32	28	1.84	NA	NiO/SiO <sub>2</sub> Nanocomposite responsible for altering the wettability in carbonate rock reservoir
	LHPN	Sst	35	<10			1.92	
[106]	NWPN		35	0	NA.	NA.	29.23	Capillary number improvement leads
	HLPN		35	NA.	_		29.01	
[107]	SiO <sub>2</sub>	Sst	12	40	17.5	7	28	Sweep efficiency improved by IFT reduction
[100]	TiO <sub>2</sub>		55.3	61.9	17.5	12.5	6.6	Transaction (1, 1, 1)
[108] -	SiO <sub>2</sub>	Carb.	54.8	57.7	16.7	11.1	2.9	lemperature affects off recovery
[109]	$\gamma$ -Al <sub>2</sub> O <sub>3</sub>	Carb.	119.8	40	NA.	NA.	11.25	$\gamma$ -Al <sub>2</sub> O <sub>3</sub> plays the main role in altering the wettability from oil to water wet
	$Al_2O_3$	Sst	53.68	28.6			NA.	As a result of nanoparticle deposition, rock surface altered to water wet
[110]	TiO <sub>2</sub>		53.68	21.6	NA.	NA.		
	SiO <sub>2</sub>		53.68	38.8				
[111]	$Al_2O_3$	_				NA.	12.5	For guaranteeing optimum oil recovery design, engineers should select the effective nanoparticle type and size
	MgO		NA. NA.				1.7	
	Ni <sub>2</sub> O <sub>3</sub>	Sst		NA.	NA.		2	
	ZnO	_					3.3	
	Fe <sub>2</sub> O <sub>3</sub>						9.2	
[112]	SiO <sub>2</sub>	Micrm.	134.4	54.52	37.5	22.1	10	Amine-functionalized silica
			134.4	23.71	37.5	13	28	typical nanoparticles
[113]	SiO <sub>2</sub>	Carb.	140.2	68.5	NA.	NA.	7.7	Disjoining pressure of SiO <sub>2</sub> was the main mechanism to remove the oil from the surface
[11/]	SiO	Set	135.5	66	26.5	1.95	25.43	SiO <sub>2</sub> is more effective for light
[114]	5102	551	130	101	28.3	7.3	14.55	oil reservoir
[115]	SiO <sub>2</sub>	Sst	NA.	NA.	NA.	NA.	5–35	Arrangement of silicon nanoparticle improves IFT
[116]	LHPN	Sst	87	28	28	7	21	Wettability is altered when polysilicon is adsorbed on the sandstone pore wall
[117]	TiO <sub>2</sub> /SiO <sub>2</sub> NCs	Carb.	138	48	39	13.2	26	Trapped oil is mobilized by the nanocomposite
[118]	LHP	Sst	NA.	NA.	14.7	9.3	2	Nanofluid was more effective for secondary recovery
[119]	TiO <sub>2</sub>	Sst	NA.	NA.	23	18	14	Low concentration of $TiO_2$ improved the oil recovery
[117]	Fe <sub>2</sub> O <sub>3</sub> /SiO <sub>2</sub> NC	Sst	138	52	39	17.5	31	Nanocomposite was able to alter wettability of the rock surface dramatically

Oil Im- provement	Remark
33	$SiO_2$ can desorb the oil from the rock
31	Higher disjoining pressure as a result of using higher concentration
8.7	

Def	Nano Type	Lith.	Contact Angle		IFT		Oil Im-	Bomoule
Kef.			Before	After	Before	After	provement %	Remark
[120]	SiO <sub>2</sub>	Sst	74	1.2	16	1.4	33	$SiO_2$ can desorb the oil from the rock
[121]	TiO <sub>2</sub>	Sst	125	90	NA.	NA.	31	Higher disjoining pressure as a result of using higher concentration
[122]	SiO <sub>2</sub>	Micrm.	100	0	NA.	NA.	8.7 (0.1 wt%) 26 (0.3 wt%)	Contact angle and IFT are dependent on the weight % of nanoparticle
[123]	TiO <sub>2</sub>	Sst	18	8	47.5	44.5	9.5–13.3	Decrease in capillary force
[124]	ZrO <sub>2</sub> and NiO	Carb.	152	44	NA.	NA.	NA.	Additional IFT reduction after using nanoparticle
	Al <sub>2</sub> O <sub>3</sub>		131	92	38.5	2.25	20.2	Dispersant agent (propanol) was used
[125]	Fe <sub>2</sub> O <sub>3</sub>	Sst	132.5	101	38.5	2.75	17.3	for the first time and was effective in
	SiO <sub>2</sub>		134	82	38.5	1.45	22.5	IFT reduction
[126]	SiO <sub>2</sub>	Carb.	NA.	NA.	NA.	NA.	8.7	By using nanoparticles, rheological properties of the displacing phase improved
					Nano-S	urfactant		
[127]	$SDS + Al_2O_3$ $SDS + ZrO_2$	Carb.	92	75 84	9.88 9.88	2.75 2.78	NA	Anionic surfactant is less effective than cationic surfactant for
[128]	NaCl + CAPB + SiO <sub>2</sub>	Carb.	156.2°	75.1°	39.63	1.10	12.2	Carbonate reservoir Decrease of IFT from 39.63 to 1.10 mN/m leads to oil improvement
[129]	$SDS + SiO_2$	Micrm.	73	11	NA	NA	13	Extra heavy oil recovery as compared to SDS alone
[130]	3.22 ZrO <sub>2</sub> + 0.50 g of CTAB	Carb.	180	32	NA	NA	10	Positive outcome is observed by surfactant and nanoparticle synergism
[121]	rhamnolipid BS-spherical + silica	Carl	112	8	NA	1.85	26.1	Spherical shape nanoparticle is more - effective than other shape nanoparticle due to uniformity
[131] ·	rhamnolipid BS-sponge + silica	Carb.	120	17	NA	1.94	25.1	
[132]	ZrO <sub>2</sub> + SDS	Carb.	152	44	NA	NA	8	From the tests, it was obvious that $ZrO_2$ is very effective in changing the wettability from oil wet limestone to water wet
[133]	SiO <sub>2</sub> + AL- FOTERRA	Carb.	167	146	23.2	7.2	10	Using nano was effective in additional oil recovery in ambient and HPHT conditions
[134]	Anionic surfactant + Al <sub>2</sub> O <sub>3</sub>	Carb.	142	0	NA.	NA.	NA	At relatively low concentrations, Al <sub>2</sub> O <sub>3</sub> can improve anionic surfactant to alter the oil wet to water wet more effectively
[129]	A <sub>2</sub> O <sub>3</sub> /SiO <sub>2</sub> + SDS, CTAB	Carb.	73	11	NA	NA	15	Small size and high surface area of nanoparticles were very effective

Ref.	Nano Type	Lith.	Contact Angle		IFT		Oil Im-	<b>B</b> ann anls
			Before	After	Before	After	provement %	Kemark
[127]	CTAB + Al <sub>2</sub> O <sub>3</sub>	Carb.	70	52	8.46	1.65	NA	Smaller particle size of Al <sub>2</sub> O <sub>3</sub> leads to higher surface energy, resulting in
	$CTAB + ZrO_2$		70	60	8.46	1.85		bigger repulsion force
[135]	$SDS + ZrO_2$	Carb.	NA	NA	48	10	NA	At and below CMS nanoparticles have a great role in IFT reduction
[136]	non-ferrous metal + anionic surfactant	Sst	23	19	31.4	9.2	12–17	Nanoparticles decrease surfactant adsorption
[27]	$ZrO_2 + SDS$	Carb.	101	30	16	3.1	25	Cationic surfactant was more effective
	$ZrO_2 + CTAB$		101	16	18.4	5.4	32.5	at altering the wettability
[64]	Cationic anionic + silica	NA	59	46	45	43	45	Nanoparticle size 5–75 was effective at reducing the IFT
[137]	SDS + ZnO	Sst	NA	NA	32.5	7.1	19	Sodium dodecyl sulphate gives better stability of ZnO
[35]	ZnO + SDBS	Sst	44.45	42.47	10.86	10.2	8.5–10.2	Decreasing in NP size leads to contact angle reduction
[138]	SiO <sub>2</sub> + Soloterra964	Sst	43.4	103.2	13.78	0.78	17.23	Nanosurfactant was a suitable EOR agent
[127]	TX-100 + Al <sub>2</sub> O <sub>3</sub>	Carb.	85	62	9.13	2.55	NA.	For carbonate, nonionic surfactant is more effective in altering the
	TX-100 + ZrO <sub>2</sub>		85	71	9.13	2.64	NA.	wettability as compared to ionic surfactant
					Nano-I	Polymer		
[139]	SiO <sub>2</sub> + 2-Poly(MPC)	Sst	NA.	NA.	47	35	5.2	Using copolymer with nano silica yielded higher oil recovery
[140]	Silica + DMAEMA	Sst	85	62.2	27	14	9.9	Nanoparticles reduce polymer adsorption
[141]	Nanoclay + HPAM	Sst	NA.	NA.	NA.	NA.	5	Improvement in viscosity after using Nanoclay/HPAM
[142]	SiO <sub>2</sub> + PAM	Sst	NA.	NA.	27	10.2	24.7	Due to disjoining pressure, oil wet is changed to water wet
[143]	SiO <sub>2</sub> + Xanthan gum	Sst	86	20	17.8	6.4	7.81	More oil is produced from unswept areas leading to improving residual oil recovery
[144]	$SiO_2 + PVP$	Sst	54	22	19.2	7.9	0-6.1	Oil recovery increases with increasing the concentration of nanoparticles due to improved adsorption ratio
[98]	$Al_2O_3 + PVP$	Sst	54	21	NA.	NA.	7–24	IFT and contact angle improved synergistically, in a nanocomposite form as compared to individual nanoparticle

Ref.	Nano Type	Lith.	Contact Angle		IFT		Oil Im-	
			Before	After	Before	After	provement %	Remark
					Nar	io-SP		
[62]	SiO <sub>2</sub> + PAM + SDS	Sst	NA.	NA.	NA.	0.13	17.49	Pressure drop increased to 0.38 MPa
[62]	Clay + PAM + SDS	Sst	NA.	NA.	NA.	0.238	18.28	Higher viscosity as compared to conventional SP
[64] -	Nanoclay + 2800 PAM + 0.2 SDS	Micrm.	. NA.	NA.	NA.	NA.	6.8	The injection of nano to SP leads to a more uniform flow pattern in a
	Nanoclay + 3000 PAM + 0.2 SDS						8	micromodel, which yields a more stable front

LHPN = lipophobic and hydrophilic polysilicon nanoparticle; HLPN = hydrophobic and lipophilic polysilicon nanoparticle; NWPN = neutral wet polysilicon nanoparticle; TX-100 = Triton X-100; PVP = Povidone: Polyvinylpyrrolidone; DMAEMA = Dimethylamino-ethyl methacrylate; CTAB = Cetyl trimethylammonium bromide; CAPB = Cocamidopropyl betaine. MPC = methacryloyloxyethyl phosphorylcholine.

This work systematically investigates the potential of NASP suspension for enhanced oil recovery (EOR) in carbonate and sandstone reservoirs. Using NASP (Nano/Alkaline/Surfactant/Polymer) could be proved successfully in future work due to its ability to improve displacement and sweep efficiency.

In the case of NASP, various mechanisms will be activated, and the interaction of them will be important, which we will describe separately to better understand the issue:

- I. The capability of the nano-polymer suspensions for improving the oil recovery by the following mechanisms:
  - 1. Wettability alteration was explored using contact angle measurement; increasing temperature and adding salt to polymeric solutions caused a reduction in shear viscosity, and the addition of NPs to the solutions could relatively recover the viscosity;
  - 2. The presence of polymers in the nanofluids improved dispersion stability of NPs;
  - 3. The nano-polymer suspensions could improve the ability of the NPs for wettability alteration and faster equilibrium states obtained than the polymer-free nanofluids.
- II. The performance of the nano-surfactant solutions for improving the oil recovery by the following mechanisms:
  - 1. The adsorption process of these substances is one of the important methods to increase the oil recovery factor from oil reservoirs by wettability alteration;
  - 2. The results of the IFT experiments of these materials showed that surfactant nanofluid solutions could significantly reduce the IFT value between the oil and water system.
- III. Alkaline can activate the following mechanisms:
  - 1. Interfacial tension reduction;
  - 2. Wettability alteration;
  - 3. Control of adsorption of ions;
  - 4. Improving the emulsion stability;
  - 5. Inhibitor of clay swelling.

Suitable experimental design is critical for using nanoparticles with chemical EOR. This paper for the first time will investigate a detailed schematic diagram for using nanoparticles in hybrid with ASP for future perspectives.



**Figure 8.** Future experimental work. The figure forecasted NASP experimental work methodology. The latter is subdivided into several sections: material preparation, carbonate rock preparation and EOR static tests (IFT and contact angle) and Dunamis tests (core flooding and micromodel).

# 12. Conclusions

- 1. To sum up, CEOR was applied to greatly increase the ultimate oil recovery by wettability, IFT and mobility modification. This paper will add a new insight integrating nano-alkaline, polymer and surfactant flooding for the first time by addressing the main mechanism of each one. The main conclusions of this paper are as follows:
- 2. ASP limitations could be due to alkaline since alkaline reduces polymer viscosity;
- 3. Due to nano, surfactant, polymer, and alkaline synergy effects, most of the EOR mechanisms are greatly improved, leading to higher oil recovery as compared to using each component alone;
- 4. The objective behind using NASP in hybrid is to modify wettability, IFT and mobility ratios, which are regarded as the main EOR mechanisms;
- 5. NASP type and concentration play a major role in changing wettability and reducing IFT to a minimum level;
- 6. For checking the mobility of chemical EOR, the micromodel is used to find the fluid flow distribution;
- 7. Nanoparticle type and size play a major role in changing wettability and reducing IFT to the minimum level;
- 8. Future recommendations by utilizing NASP will probably be a new finding to understand the details about the EOR system in both micro- and -macroscale settings;
- 9. This review paper highlights the fact that natural surfactants are less costly, biodegradable, available, less toxic, more stable, and environmentally friendly, and it can reduce the IFT to an ultra-low value.
- 10. NASP could effectively boost the oil recovery by more than 25% due to the synergism effect.

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